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ESR SPECTRA OF THE PLEIADIENE ION RADICALS

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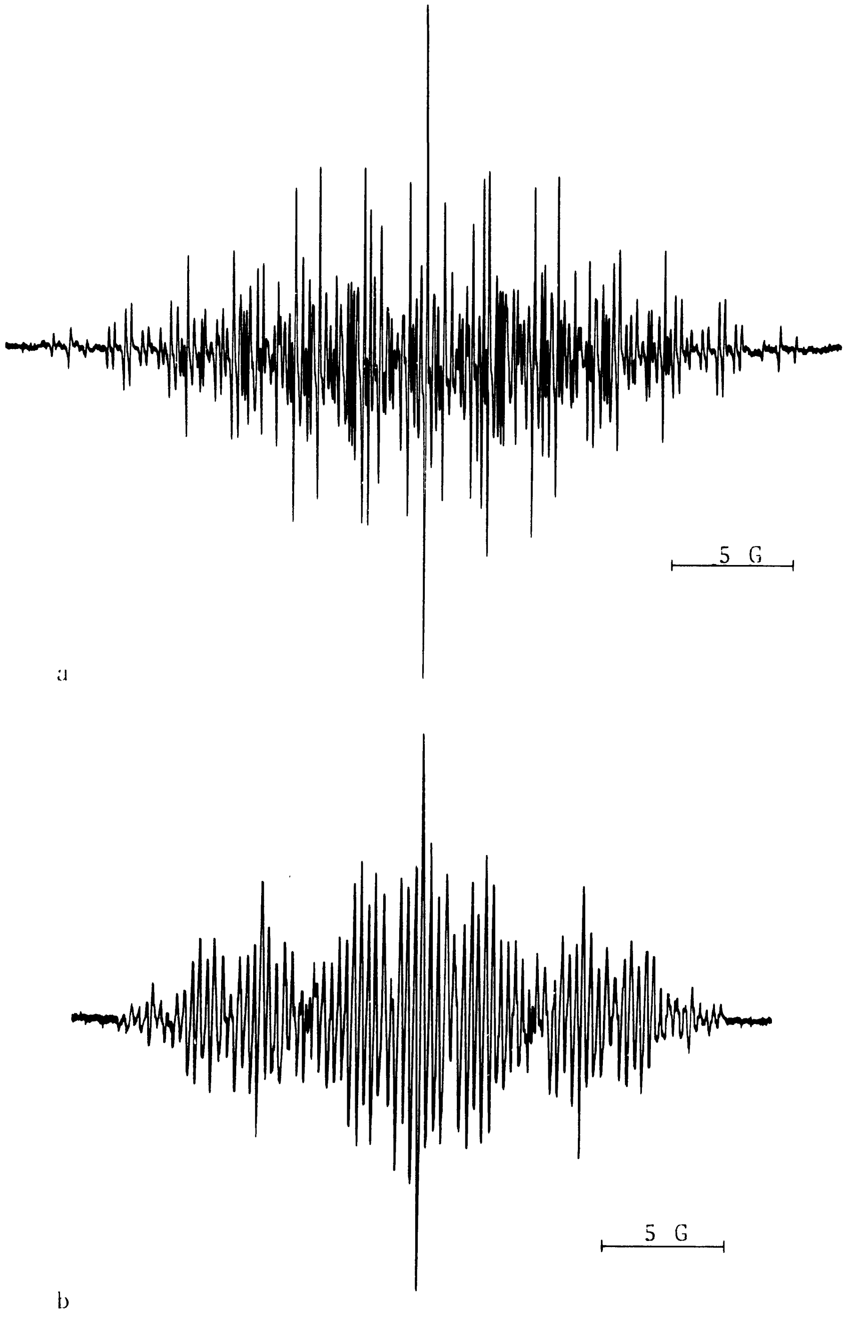
Treatment of pleiadiene with concentrated sulfuric acid generated the cation radical which exhibited a strong ESR signal. The anion radical of pleiadiene was produced by the treatment with an alkali metal. Hyperfine splitting constants for both ion radicals were discussed with the MO calculations.

Pleiadiene (I) is a typical nonbenzenoid aromatic compound and has been of interest to many investigators.1-7) The electron spin resonance (ESR) study of this compound was first reported by Nelsen and Gillespie6) for the anion radical generated by the electrolytic reduction in dimethylsulfoxide or by the reduction with sodium-potassium alloy in tetrahydrofuran. We are very much interested in the cation radical of I with a view that the ESR spectra of the cation and anion radicals are expected to be dissimilar for such a nonalternant hydrocarbon. The study was carried out after a novel preparation of I through the reaction of phenalene with n-butyllithium in dichloromethane.7) This paper reports the ESR spectrum of the cation radical together with our experiments on the anion radical.

Dissolution of a small amount of pleiadiene reddish orange crystals in a few drops of concentrated sulfuric acid readily produced a deep red solution which exhibited a strong ESR signal with hyperfine splittings. The spectrum is shown in Fig. 1a. The cation solution was stable for a couple of weeks at room temperature. Hyperfine structure of the spectrum was analyzed with five splitting constants given in Table 1 which were confirmed by the spectral simulation with a computer. Careful treatment of I with sodium metal in tetrahydrofuran (THF) resulted in a disappearance of its orange color. The solution was stable for a few days at room temperature, showing the ESR spectrum of Fig. 1b. Five splitting constants given in Table 1 were afforded by the spectral analysis. The anion radical was also obtained by the treatment of I with potassium metal in 1,2-dimethoxyethane (DME), but the splitting constants are slightly different from those of the above Na-THF solution and from those obtained electrolytically in dimethylsulfoxide.6)

Assignment for the splitting constants can be made by comparing them with the calculated spin densities, as given in Table 1. It is noteworthy for both



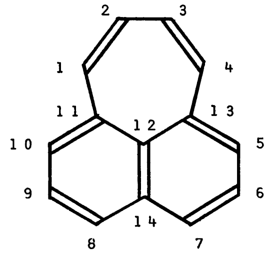


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Fig. 1. ESR spectra of the cation radical (a) and the anion radical (b) of pleiadiene.

spectra that the total extents for the cation and anion radicals are quite different; 31.0 G for the cation and 24.6 G for the anion. Dissimilarity of the splitting constants for both ion radicals is also noticeable. These are reasonably explained by the fact that the lowest antibonding orbital, ψ_a, and the highest bonding orbital, ψ_b, which are paired in alternants, are non-paired in such nonalternant hydrocarbons. The squared LCAO coefficients of the two frontier orbitals at each carbon atom are different for nonalternants. The

Table 1. Observed Splitting Constants ($\underline{a}_i$) and Calculated Spin Densities (ρ_i) for the Pleiadiene Cation and Anion Radicals

Position	Cation radical				Anion radical			
	$\underline{a}_i$	ρ_i			$\underline{a}_i$	ρ_i		
		Exptl.[a]	Calcd.[b]			Exptl.[a]	Calcd.[b]	
	G		Hückel	McLachlan	G		Hückel	McLachlan
1, 4	2.56	0.095	0.1042	0.1193	6.59	0.275	0.2384	0.2905
2, 3	2.33	0.086	0.0677	0.0634	2.55	0.106	0.1122	0.0917
5, 10	4.46	0.165	0.1345	0.1711	0.93	0.039	0.0323	0.0316
6, 9	0.70	0.026	0.0088	-0.0370	0.31	0.013	0.0009	-0.0182
7, 8	5.45	0.202	0.1516	0.1917	1.92	0.080	0.0374	0.0395
11, 13			0.0332	0.0147			0.0125	-0.0111
12			0.0000	-0.0079			0.1293	0.1676
14			0.0000	-0.0384			0.0035	-0.0157

a) With the relation $\underline{a}_i = \underline{Q}_{CH}^{H} \times \rho_i$, in which $|\underline{Q}_{CH}^{H}|$ = 27 G for the cation and 24 G for the anion were adopted.

b) λ = 1.0 in McLachlan procedure.

absence of pairing property should be reflected in the dissimilarity of the coupling constants for two ion radicals. The different spectral ranges for two corresponding ion radicals of pleiadiene can be predicted from the difference in sums of the squared LCAO coefficients at proton-bearing centers μ ($\Sigma c_{a,\mu} = 0.842$ and $\Sigma c_{b,\mu} = 0.934$ with Hückel MO).

The Hückel MO calculations with the approximate configuration interaction treatment of McLachlan were applied for the spin density estimation for both ion radicals. The results are included in Table 1. The fit of the calculations with the experimental values is not very good for either Hückel and McLachlan procedures, but is enough for the assignments of the splitting constants. The assignments accord with those for the ring protons in the acepleiadiene ion radicals.[3)] To find out better agreement between the calculated and experimental densities, further calculations were attempted taking reduced resonance integrals for some C-C bonds into consideration, in which (a) reduced resonance between naphthalene and butadiene moieties, (b) reduced aromaticity with bond alternation, and (c) a perimeter resonance form with reduced resonance toward the central carbon atom were assumed. However, the results did not show excellent agreements for both ion radicals. Other procedure for the spin density estimation, using a method such as the INDO method, is under consideration.

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